a-Si:H/a-Si:H stacked cell with 9% stabilised efficiency deposited in a single-chamber reactor at high rate due to VHF-GD

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Abstract
In the present paper the authors present results on a-Si:H/a-Si:H stacked cells deposited in a single-chamber reactor by the very high frequency - glow discharge (VHF-GD) deposition technique at 70 MHz. Hydrogen dilution of the i-layer yields more stable amorphous p-i-n solar cells, similar to what is observed for RF deposition at 13.56 MHz plasma excitation frequency. Regarding the stacked cell design, the authors show by experiment and simulation that it is important to carefully adjust the current mismatch between the component cells such as to obtain a slight top-cell-limited behaviour after degradation. The authors present an a-Si:H/a-Si:H stacked cell with an initial efficiency of 9.8 % showing only 8 % relative degradation; this results in a stabilised efficiency of 9 % as confirmed by an independent laboratory. The deposition rate of the employed H_2-diluted i-layer material is 4 Å/s. It is therefore demonstrated that it is possible to make highly efficient stacked cells showing good stability also in a single-chamber system and employing the VHF technique to obtain higher rates.
Keywords: stability - 1: stacked solar cells - 2: rapid growth - 3.

1. Introduction

The VHF deposition technique at 70 MHz has shown to yield much higher growth rates than those obtained for "standard" 13.56 MHz plasma deposition [1]; this becomes even more important in the case of H_2-dilution (as used to obtain i-layers with higher stability), where deposition rates generally strongly decrease. However, the question persisted as to whether cells obtained from VHF deposition at higher growth rates would be as stable as "slowly" grown cells from "conventional" RF deposition at 13.56 MHz. In fact, for RF deposition, an increase in deposition rate by means of increased input power or a change of the plasma regime is found to be harmful for the stability of the solar cells [2-6]. In the present paper, the authors present an a-Si:H/a-Si:H stacked cell deposited in a single-chamber reactor with the VHF deposition technique which has 9% stabilised efficiency after a relative degradation of only 8%. The i-layer of this cell has been deposited at a rate of 4 Å/s.

2. Hydrogen dilution for enhanced stability

Hydrogen (H_2)-dilution has been shown to increase the stabilised efficiency of a-Si:H solar cells due to more stable i-layers [7]. In a previous work, we have shown that, for the VHF deposition technique, also, H_2-dilution yields enhanced stability against light-soaking [8]. However, strong H_2-dilution was found to reinforce contamination problems. This issue will be addressed in the following.

2.1. Contaminations

Contamination problems can be divided into two groups: The first group are problems due to the single chamber system, i.e. mainly cross-contamination by the doping gases; the second group are problems which can also appear in multichamber systems. In this second group, we have to deal mainly with oxygen originating from different sources. We found both groups of problems to become much more important when depositing i-layers under H_2-dilution.

Having reduced to a large extent the outgassing rate of the reactor as the main source of oxygen contamination, by heating the chamber walls overnight and cooling down before deposition, a part of the oxygen problem still remained. We attributed the remaining contamination to impurities in the feedstock gases and therefore employed a gas-purifier [9]. Thereby, the reduced collection efficiency for red light (which is an indication for n-type contamination [10]) could be further reduced. Fig.1. shows the collection efficiency (=SR(0V)/SR(-3V)) of three 450 nm thick solar cells where the i-layer has been deposited with a strong H_2-dilution. Curve "1" corresponds to a cell deposited without gas purifier, curve "2" is that of the same cell, where a gas purifier has been employed for the i-layer. Note that the i-layer thickness is 450 nm. For thinner cells, the reduction in collection is less pronounced, thanks to the strong internal electric field, prevailing here. For curve "2" (Fig.1.), the red collection efficiency is better than for curve "1" but not yet sufficiently high; we attribute this remaining imperfection to phosphorus contamination of the i-layer. This is a problem that typically appears in single chamber reactors, only. In the past, we deposited a "dummy layer" after the n-layer of a cell which covers the electrodes and prevents from phosphorous contamination of the next cell. This worked very well for cells deposited from undiluted or only slightly H_2-diluted SiH_4-plasma. When depositing the i-layer from a highly H_2-diluted plasma, we obtained an n-doping effect in the i-layer in spite of the dummy deposition. In fact, the strongly reactive H_2-plasma reaches uncovered parts of the reactor or parts which had been covered only with a thin dummy layer and etches the material containing phosphorus which afterwards is incorporated into the i-layer. Conclusively, we next made the dummy layer also with a strongly diluted SiH_4-plasma and at the very low pressure of 0.2 mbar. In this case the plasma is burning also outside the electrodes and covers all parts which can be reached afterwards by the i-layer-plasma. Thereby we obtained a further reduction of the collection losses in the red wavelength region as indicated by curve "3" in Fig.1. and a fill factor for the 450 nm thick cell of 70 %. From Fig.1. one can further see that the collection of blue light is reduced as soon as the strong oxygen-contamination is taken away. This is obviously due

to boron contamination which is now no more compensated by oxygen or phosphorus. Boron contamination appears once again mainly in the case of single-chamber reactors. However, also for multi-chamber systems, such boron contamination from the substrate holder is sometimes reported. After the deposition of the p-layer we take the substrate out of the chamber into the loadlock. A CO_2-plasma at relatively high pressure (1 mbar) and high power efficiently removes boron from the chamber [11] when the i-layer is deposited without dilution or with only small H_2-dilution ratios. However, when a strong H_2-dilution is employed for the successive i-layer deposition, we find boron contamination in the i-layer which is detected by a decreased collection for blue light. If one operates the CO_2-Plasma at the same chamber pressure as the p-layer deposition (0.3 mbar), the problem is decreased to a certain amount; nevertheless, there seems to be still some boron in the first part of the i-layer. We assume that this could be due to an etching of the p-layer during the deposition by the highly diluted i-layer plasma. An indication to support this hypothesis is that we need about 150 % of the normal p-layer thickness when employing high H_2-dilution for i-layer deposition in order to obtain maximum V_{OC}. Note that the optical transmission of the p-layer is not diminished hereby; this could indicate an etching of the p-layer during the first seconds of i-layer deposition. Such a behaviour has, to our knowledge, not yet been reported for RF (13.56 MHz) deposition, whereas for VHF deposition etching has already been observed under certain conditions [12].

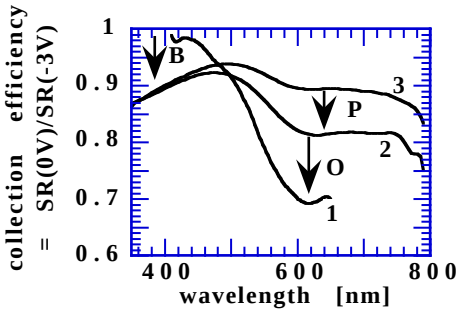

Figure 1: Effect of different contaminations on the collection efficiency of a 450 nm thick p-i-n solar cell. Substrate temperature was 180°C, the i-layer was deposited with a dilution ratio of 9.
Curve 1: Using a dummy layer from an undiluted silane plasma after n-deposition. Curve 2: Additionally, a gas purifier was used eliminating a large part of the oxygen contamination. Curve 3: The dummy layer after n-deposition was made using a strong H_2-dilution and low chamber pressure (0.2 mbar) thereby reducing the phosphorous contamination. Boron contamination is hidden behind strong O- or P- contamination.

2.2. Optimised single-junction cells

Having at least partly resolved the problems due to contaminations, the question arised which amount of dilution is necessary w.r. to stability and useful w.r. to the increase in the optical gap. We found that a relatively thin layer with the highest gap (=highest dilution) at the p-i-interface only is sufficient to achieve the maximum possible V_{OC} similar to what is reported in [13]. Therefore, we developed cells with a graded dilution ratio in the i-layer. The first part of the i-layer of about 30 nm close to the p-i-interface was deposited with the high dilution ratio of 9 (at 2 Å/s). The rest was deposited using a dilution ratio of 2 (at 4 Å/s). We could thereby combine a good i-layer stability (dilution ratio 2 of the bulk), avoid a too strong increase of the optical gap (the optical gap increases with increasing H_2-dilution ratio) and still obtain a high V_{OC}. Fig.2a. shows the V_{OC} and FF values of such cells with graded-dilution i-layers in the initial and degraded state for 3 different i-layer thicknesses, Fig.2b. the short circuit currents and the resulting efficiency values. The gain in V_{OC} and the better stability of the fill factor value is to some extent counteracted by a loss in the optical absorption due to an increase of the optical gap under H_2-dilution. After 1000h light-soaking, all cells show, independently of the cell thickness, an efficiency of about 7.5 %. In fact, the increase in current with increasing i-layer thickness is compensated by a stronger fill factor degradation.

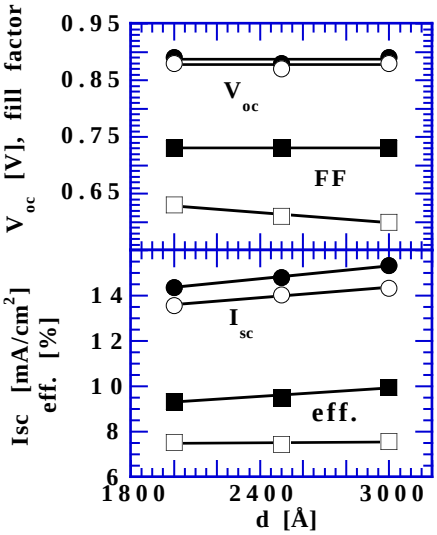

Figure 2a: Measured values of V_{OC} and FF in the initial (black symbols) and degraded (1000 h, open symbols) state for single-junction cells with graded-dilution i-layers and different i-layer thicknesses. T_S=180°C.
Figure 2b: I_{SC} and efficiency in the initial and degraded (1000 h) state for the cells of Fig.2a.

Due to their high V_{OC}, only slightly reduced short circuit current, and excellent stability, these cells with a graded hydrogen dilution ratio have already been successfully incorporated as top cells in micromorph tandem cells resulting in 10.7% stabilised efficiency as confirmed by the Fraunhofer Institute (FhG-ISE) at Freiburg (D) [14,15].

3. Optimising the stacked cell

3.1. General considerations

It has been shown that it is possible to reduce light-induced degradation by making the stacked cell top-limited [16]. The following simple modelling shows that, in fact, a stacked cell has the highest output power if its current is limited by the top-cell in the degraded state. The modelling is based on measured I-V-curves of single-junction p-i-n cells in different states of degradation. In order to estimate the I-V-curve of a stacked cell we simply added the V(I) curves of the both component cells. The current values of the component cells were scaled before by a constant factor in order to obtain the desired current mismatch, the total cell current was held constant at 15 mA/cm^2. Scaling was

done at I(-2V), thereby including the current degradation for degraded cells into the model.
Fig.3a. shows the dependence of the output power of the stacked cell (=V_{OC}·I_{SC}·FF) as a function of the current mismatch for different pairs of top and bottom cells. For two cells with the same fill factor, the maximum output power is obtained for matched cell currents. In a stacked cell, however, the bottom cell will always degrade to a larger extent than the thinner and more stable top cell. Thus, if we pair a high-FF top cell with a bottom cell showing a lower fill factor, we observe a shift of the point of maximum power towards slightly top-limited conditions (to the left in Fig.3a.). The model indicates that the optimum mismatch is found somewhere below a difference in current of 1 mA/cm^2, depending on the fill factors of both the top and the bottom cell. For realistic conditions we expect an optimum mismatch to be around 0.5 mA/cm^2.
Fig.3b. shows the FF values for the same conditions as in Fig.3a. For a high degree of mismatch, one can obtain very high FF values, however the power is low because of a small cell current. Also shown in Fig.3b. are measured FF values for stacked cells in the initial and degraded state. The model fits the measured values astonishingly well.

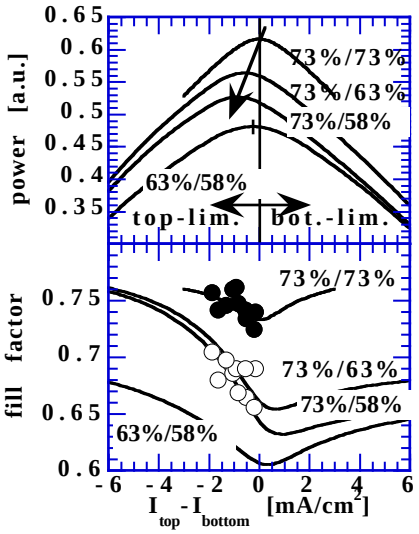

Figure 3: Modelled output power (a) and fill factor (b) values for a-Si:H/a-Si:H stacked cells as a function of the "mismatch", i.e. of the difference in (saturated) current density between top and bottom cell. The total cell current density $I_{top}+I_{bottom}$ was held constant at 15 mA/cm^2. Percentage values next to the curves mean fill factors of the top/bottom cell; e.g. 73%/58% means 73% FF for the top and 58% FF for the bottom cell.
Also shown are experimental fill factor values in the initial (black symbols) and degraded (1000h, open symbols) state for a set of 10 a-Si:H/a-Si:H stacked cells deposited at T_S = 180°C/220°C for the top/bottom cell.

Thus, in order to have a maximum power output after degradation, it is necessary to maintain top-limited conditions after degradation, as has been shown. The FF of the bottom cell is smaller than that of the top cell because of the large difference in thickness between the two cells. (The thickness of the top cell is 50-80 nm, whereas the bottom cell thickness is around 300 nm.) Furthermore, the top cell is made from strongly diluted i-material, whereas the bottom cell contains mainly undiluted material (see below). As a consequence, the top cell nearly does not degrade whereas the bottom cell suffers relatively strong degradation.

3.2. Technological realisation

Whereas for the top cell in a tandem or stacked structure the loss in absorption due to H_2-dilution can easily be compensated by an only slightly thicker i-layer, the situation is more difficult for the bottom cell in an a-Si:H/a-Si:H cell without germanium alloying. Its current must be large enough to at least match the current of the top cell.
Taking as a goal an initial efficiency of 10 %, one needs with a V_{OC} of 1.75 V and a fill factor of 74 % a current of 7.7 mA/cm^2. This means at least 8 mA/cm^2 for the bottom cell in the initial state in order to maintain top-limited conditions after degradation. This is not achievable with a diluted i-layer in the bottom cell and at low temperature (180°C). Therefore, we deposited the bottom cell at "standard" temperature (220°C) and without H_2-dilution. Again, a thin "buffer layer" of diluted material was inserted at the p-i-interface, increasing thereby the V_{OC} of the bottom cell. By employing this technique of depositing bottom and top cells at different temperatures, the bottom cell provides enough current and can still be "rather thin".

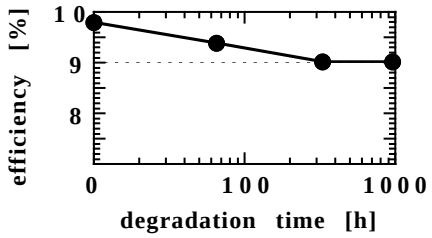

Figure 4: Measured degradation kinetics of the a-Si:H/a-Si:H stacked cell. Saturation appears after 300h of light-soaking at 50°C under open-circuit conditions.
initial: 1.73V, 74%FF, 7.65mA/cm^2, 9.8% (IMT)
1000h: 1.71V, 69%FF, 7.64mA/cm^2, 9.0% (IMT)
FhG-ISE (1000h): 1.7V, 66%FF, 7.7mA/cm^2, 8.6±0.6%.

We deposited such a 2-temperature p-i-i-n-p-i-i-n stacked cell. Its initial efficiency is 9.8 %, after 300h degradation the efficiency stabilises at 9 % (8.6±0.6 % according to the measurement by the Fraunhofer Institute (FhG-ISE) at Freiburg (D)) which means a relative degradation of only 8 % (Fig.4.). Degradation is partly due to V_{OC}, the stabilised fill factor of 69 % is quite high. The cell has a current mismatch of 0.56 mA/cm^2 in the initial and of about 0.3 mA/cm^2 in the degraded state which confirms the above considerations that the highest stabilised power can be achieved by a slight current mismatch for component cells with different fill factors.

4. Enhanced deposition rates due to VHF-GD

The VHF deposition technique at 70 MHz has shown to yield much higher growth rates than “standard” 13.56 MHz deposition. This becomes even more interesting in the case of H_2-dilution for the deposition of more stable i-layers where deposition rates generally strongly decrease. Fig.5. shows the deposition rates for VHF deposition (70 MHz) and different dilution ratios at T_S=180°C. The deposition rate decreases approximately linearly with dilution, starting from the rather high value of 4.5 Å/s at 4 W (30 mW/cm^2) input power (measured between generator and matching network, not corrected for network losses). At a dilution ratio of 9 we still obtain a deposition rate of over 2 Å/s.

The input power density of 30 mW/cm^2 has been chosen arbitrarily, it is possible to deposit material at higher rates by increasing the input power as shown in Fig.5. There is no difference in degradation in between cells incorporating the 4 W or the 8 W material. Especially at high H_2-dilution ratios, the decrease of deposition rate can become a problem for efficient industrial production. Fig.5. shows for comparison deposition rates for different dilution ratios and RF (13.56 MHz) deposition. The values are taken from [17]. Other laboratories also report values around [18] or below 1 Å/s [19], depending on the dilution ratio of the i-layer. Our 9% stable stacked cell has been deposited at a rate of 4 Å/s for the top and 6 Å/s for the bottom cell. A comparable RF-deposited 9% stable cell [20] has been deposited at 1 Å/s and 1.5 Å/s for the top and bottom cell respectively [21].

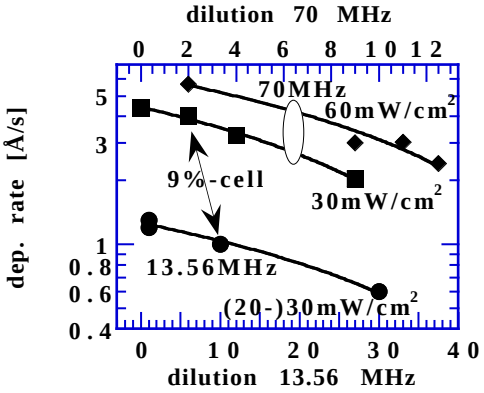

Figure 5: Comparison of deposition rates for 70 MHz (VHF) and conventional 13.56 MHz [17] deposition in function of the H_2-dilution ratio. The H_2-diluted top cell i-layer of a 9% stable stacked cell has been deposited at 4 Å/s in our case and at 1 Å/s in the case of 13.56 MHz deposition [20].

Total process time including 20 minutes of substrate pre-heating is 98 min. For the deposition alone, including the H_2-diluted i-layers, we need only 22 min.; this low value is obtained by employing the VHF deposition process. Schropp et al. [22] report for a stacked cell deposited also in a single-chamber (but at 13.56 MHz) a deposition time of at about 130 min. without any cleaning step in between doped and intrinsic layers and without H_2-dilution for the i-layers.

5. Conclusions

Hydrogen dilution and an appropriate design of the p-i-n cell yields solar cells with high initial and stabilised efficiencies. We have shown that in a single chamber reactor also, solar cells showing gooed efficiencies can be fabricated if contaminations are counteracted by appropriate measures.

The VHF deposition technique at 70 MHz yields remarkably increased deposition rates as compared to conventional RF deposition. This is even more interesting for H_2-diluted layers as deposition rates generally decrease strongly with the H_2-dilution ratio. Pure deposition time for our a-Si:H/a-Si:H stacked cell including H_2-diluted layers is 22 min., the diluted i-layer being deposited at 4 Å/s (although "even higher" values seem feasible).

High stabilised efficiency values can be achieved for a-Si:H/a-Si:H stacked cells if the current mismatch between the top and the bottom cell is maintained after degradation. In order to provide enough current for the bottom cell, we deposited the bottom cell at a higher temperature (220°C) than the top cell (180°C). The necessary short heating-up of the top cell before and during bottom cell deposition has no adverse effect on the top cell properties. A combination of 2 different dilution ratios in both i-layers yields a combination of high V_{OC} values, sufficient current and good stability.

We presented an a-Si:H/a-Si:H stacked cell with an initial efficiency of 9.8 % and a stabilised efficiency of 9 % which had been deposited in a single chamber using the VHF deposition technique at 70 MHz. This result is comparable to stabilised efficiencies for a-Si:H/a-Si:H cells without germanium alloying of laboratories using multichamber systems and 13.56 MHz RF-deposition. It is therefore demonstrated that it is possible to make highly efficient stacked cells showing good stability also in a single-chamber system and employing the VHF technique to obtain higher deposition rates.

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